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THERMODYNAMICS OF SILVER–SILVER HALIDE ELECTRODES AND THERMODYNAMIC SOLUBILITY PRODUCTS OF SILVER HALIDES IN GLYCEROL + WATER MIXTURES AT DIFFERENT TEMPERATURES

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ABSTRACT

The standard potentials of silver–silver bromide and silver–silver iodide electrodes in glycerol + water mixtures containing 5, 10, 20 and 30 wt% glycerol were determined from electromotive force measurements of the cell Ag(s), AgX(s), KX(c)//KCl(c), AgCl(s), Ag(s), where X is Br or I, at seven different temperatures in the range 5–35°C. The standard potentials in each solvent are represented as a function of temperature. The standard thermodynamic functions for the electrode reactions, the primary medium effects of various solvents upon X^-, and the standard thermodynamic quantities for the transfer of 1 g-ion of X^- from water to the respective glycerol + water media are evaluated and discussed in the light of ion–solvent interactions as well as the structural changes of the solvents. From the values of the Ag/Ag^+ and $Ag/AgX, X^-$ electrodes, the thermodynamic solubility product constants of silver chloride, silver bromide and silver iodide have been determined in glycerol + water solvent mixtures at different temperatures.

INTRODUCTION

The standard potentials of the silver–silver bromide and silver–silver iodide electrodes were determined by Khoo [1] in 10, 20, 30, 40, 50, 60 and 70 wt% glycerol + water mixtures at 25°C using the cell $H_2|HX|AgX–Ag$ (X = Cl, Br or I).

As a continuation of the study to determine the standard potentials of the first and second type electrodes in aqueo-organic solvents [2], measurements of the EMF of cell (A)

$$Ag(s), AgX(s), KX(c)//KCl(c), AgCl(s), Ag(s) \qquad (A)$$

where X is Br or I, were made in 5, 10, 20 and 30 wt% glycerol + water mixtures and extended to cover a sufficiently wide range of temperatures. The standard potentials of the silver–silver bromide and silver–silver iodide electrodes are reported in glycerol + water mixtures at seven different temperatures ranging from 5 to 35 °C. In addition, the relevant thermodynamic functions for the X^- ion and the thermodynamic solubility product constants of AgX (X = Cl, Br or I) are evaluated in these solvent mixtures at different temperatures.

EXPERIMENTAL

The preparation of the silver–silver chloride, bromide or iodide electrodes has been described earlier [3]. Only those electrodes which showed a potential difference of $\leqslant 0.1$ mV in comparison with another electrode of the same type were used. The cell vessels were of an all-glass design as previously described [2].

Potassium chloride, bromide or iodide was of analytical grade and used without further purification. Glycerol (BDH, Laboratory reagent) was purified by a previously described method [2g]. Solvents of various composition were made up by weight in conductivity water.

Equimolar solutions of potassium halides were prepared from the stock solutions by the double dilution method. The general experimental procedures for setting up the cells, the EMF and conductance measurements were essentially similar to those described earlier [2]. All measurements were made in the water thermostat maintained at ±0.1 °C. The reproducibility of EMF measurements was of the order of ±0.2 mV.

RESULTS AND DISCUSSION

As usual [2], the standard molar potentials, E_c^0, of the silver–silver bromide and silver–silver iodide electrodes were obtained by the method of extrapolating [2] the auxiliary function [2a]

$$E_c^{0\prime} = E^0_{\mathrm{Ag,AgCl}} - E - (RT/F)\ln([\mathrm{Cl}^-]\gamma_{\mathrm{Cl}^-}/[\mathrm{X}^-]\gamma_{\mathrm{X}^-}) + E_{\mathrm{j}}$$
$$= E_c^0 + \mathrm{f}(c) \qquad (1)$$

where the symbols have their usual meanings, to the molarity $c = 0$.

The values of the liquid junction potential, E_{j}, were calculated from the equivalent conductances of potassium chloride and potassium bromide or iodide by means of the Lewis and Sargent equation [2b]. It was found that the values of E_{j} varied in the range 0.1–0.3 mV in all solvents for all temperatures. The values of $E^0_{\mathrm{Ag,AgCl}}$ (molar scale) needed for the calculation of $E_c^{0\prime}$ (eqn. 1) at different temperatures and in various glycerol + water mixtures, were taken from the literature [4]. The logarithm term in eqn. (1) tends to zero assuming that the ratio of concentrations and activity coefficients is unity [5], since the concentrations in both sides of the cell are

TABLE 1

Standard molar potentials (E_c^0 in abs. V) for Ag/AgX, X^- electrodes in glycerol + water mixtures from 5 to 35 °C

Wt% glycerol	t (°C)						
	5	10	15	20	25	30	35
X = Br							
5	0.0806	0.0786	0.0765	0.0739	0.0713	0.0688	0.0663
10	0.0773	0.0754	0.0734	0.0714	0.0688	0.0666	0.0645
20	0.0735	0.0708	0.0682	0.0661	0.0637	–	–
30	0.0659	0.0637	0.0611	0.0591	0.0571	0.0549	0.0524
X = I							
5	−0.1474	−0.1485	−0.1496	−0.1509	−0.1521	−0.1537	−0.1554
10	−0.1478	−0.1491	−0.1505	−0.1519	−0.1533	−0.1544	−0.1560
20	–	–	−0.1509	−0.1529	−0.1551	−0.1571	−0.1595
30	–	−0.1523	−0.1543	−0.1566	−0.1586	−0.1606	−0.1630

identical. The values of E_c^0 obtained on extrapolating $E_c^{0\prime}$ to $c = 0$ are presented in Table 1. The average standard deviations in the values of E_c^0 are ± 0.3 mV.

As previously [2a], the standard potentials on the molal (E_m^0) and mole-fraction (E_N^0) scale were calculated from the E_c^0 values. The E^0 values on different scales at various temperatures for any solvent were fitted by the method of least-squares, to the equation

$$E_x^0 = a + b(t - 25) + c(t - 25)^2 \tag{2}$$

where $x = c$, m or n, and t is any temperature (°C). The constants a, b and c of eqn. (2) are presented in Table 2. The average deviations between the experimental values (Table 1) and those calculated from eqn. (2) are within ± 0.3 mV. The E^0 values at 25 °C are shown in Table 3 along with those in water [1] and glycerol + water mixtures [1] for the sake of comparison. Table

TABLE 2

Constants of eqn. (2) for molar (c), molal (m) and mole-fraction (N) scales in glycerol + water mixtures

Wt% glycerol	x	Constants		
		a	$-b \times 10^4$	$c \times 10^6$
X = Br				
5	c	0.0714	4.967	−2.0
	m	0.0707	4.73	−2.0
	N	−0.1337	11.60	−2.0
10	c	0.0688	4.394	−0.667
	m	0.0677	4.359	−0.50
	N	−0.1344	11.04	0
20	c	0.0637	4.5	2.0
	m	0.0613	4.55	2.0
	N	−0.1362	11.20	2.0
30	c	0.0570	4.64	−1.2
	m	0.0533	4.65	−0.8
	N	−0.1388	11.08	−0.8
X = I				
5	c	−0.1522	2.9	−2.667
	m	−0.1531	2.773	−2.4
	N	−0.3572	9.44	−2.4
10	c	−0.1533	3.0	−1.333
	m	−0.1544	2.7	−1.333
	N	−0.3566	9.5	0
20	c	−0.1550	4.4	−1.333
	m	−0.1575	4.4	−1.333
	N	−0.3549	11.05	−0.667
30	c	−0.1586	4.8	−2.0
	m	−0.1621	4.445	−2.5
	N	−0.3548	10.875	−1.5

3 also includes the E^0 values of the silver–silver chloride electrode in various glycerol + water mixtures [1,4] at 25 °C.

The standard thermodynamic quantities (ΔG^0, ΔS^0 and ΔH^0) on the molal scale for the electrode reaction

$$\mathrm{AgX(s)} + \mathrm{e} \rightleftharpoons \mathrm{Ag(s)} + \mathrm{X^-(solvated)}$$

and the standard thermodynamic quantities, ΔG_t^0, ΔS_t^0 and ΔH_t^0 for the transfer process $\mathrm{X^-}$(in water) → $\mathrm{X^-}$(in glycerol + water) were evaluated at different temperatures for various solvents by the usual relationships [2a]. These values are also shown in Table 3. As before [2], the transfer thermodynamic quantities were evaluated on the mole-fraction basis. Table 4 lists these values at 25 °C along with the values of the change in electrostatic Gibbs energy ($\Delta G^0_{\mathrm{t,el}}$), the electrostatic entropy ($\Delta S^0_{\mathrm{t,el}}$) and the electrostatic contributions to the change of enthalpy ($\Delta H^0_{\mathrm{t,el}}$).

To estimate the $\Delta G^0_{\mathrm{t,el}}$ and $\Delta S^0_{\mathrm{t,el}}$ values, the equations

$$\Delta G^0_{\mathrm{t,el}} = (Ne^2/2)(\epsilon_{\mathrm{s}}^{-1} - \epsilon_{\mathrm{w}}^{-1})(r_+^{-1} + r_-^{-1}) \tag{3}$$

and

$$\Delta S^0_{\mathrm{t,el}} = (-Ne^2/2)(\epsilon_{\mathrm{s}}^{-1}\theta_{\mathrm{s}}^{-1} - \epsilon_{\mathrm{w}}^{-1}\theta_{\mathrm{w}}^{-1})(r_+^{-1} + r_-^{-1}) \tag{4}$$

TABLE 3

Values of the standard potentials of the Ag/AgX, $\mathrm{X^-}$ (X = Cl, Br or I) electrodes on the molar (E_c^0), molal (E_m^0) and mole-fraction (E_N^0) scales in glycerol + water mixtures, and thermodynamic quantities on the molal scale at 25 °C (ΔG_m^0 and ΔH_m^0, J mol^{-1}, and ΔS_m^0, J mol^{-1} K^{-1})

	Wt% glycerol				
	0	5	10	20	30
X = Cl [1,4]					
E_c^0 (V)	0.2222	0.2201	0.2175	0.2119	0.2059
E_m^0 (V)	0.2224	0.2193	0.2162	0.2095	0.2022
E_N^0 (V)	0.0160	0.0151	0.0141	0.0121	0.0100
X = Br					
E_c^0 (V)	0.0709	0.0714	0.0688	0.0637	0.0570
E_m^0 (V)	0.07105	0.0707	0.0677	0.0613	0.0533
E_N^0 (V)	−0.13528	−0.1337	−0.1344	−0.1362	−0.1388
$-10^{-3}\,\Delta G_m^0$		6.821	6.532	5.915	5.143
$-10^{-3}\,\Delta H_m^0$		20.423	19.067	18.998	18.514
$-\Delta S_m^0$		45.64	42.06	43.90	44.87
X = I					
E_c^0 (V)	−0.15259	−0.1522	−0.1533	−0.1550	−0.1586
E_m^0 (V)	−0.15244	−0.1531	−0.1544	−0.1575	−0.1621
E_N^0 (V)	−0.35882	−0.3572	−0.3566	−0.3549	−0.3548
$10^{-3}\,\Delta G_m^0$		14.773	14.898	15.197	15.641
$10^{-3}\,\Delta H_m^0$		6.799	7.135	2.545	2.86
$-\Delta S_m^0$		26.757	26.053	42.456	42.89

were employed, where the radius of the silver ion (r_+) may be taken as 0.126 nm [6], that of the bromide ion (r_-) as 0.196 nm [7], and that of the iodide ion (r_-) as 0.219 nm [7]. Assuming that the radii of the ions do not change with the change of solvent [6], ϵ_s and ϵ_w are the dielectric constants of the mixed solvent and water, respectively, and were taken from the literature [8]. The values of θ_w and θ_s, the temperature coefficients of the dielectric constants, were obtained from the literature [2h]. The values of $\Delta H^0_{t,el}$ were computed from the known values of $\Delta G^0_{t,el}$ and $\Delta S^0_{t,el}$. The chemical contributions of the Gibbs free energy of transfer ($\Delta G^0_{t,ch}$), entropy of transfer ($\Delta S^0_{t,ch}$), and the enthalpy of transfer ($\Delta H^0_{t,ch}$) were obtained from the equation [2]

$$\Delta R^0_t = \Delta R^0_{t,el} + \Delta R^0_{t,ch} \qquad (5)$$

where $R = G$, S or H. These values at 25 °C are presented in Table 4.

An inspection of Table 3 shows that the standard electrode potentials of the silver–silver bromide and silver–silver iodide electrodes in various

TABLE 4

Thermodynamic quantities for the transfer process X^- (in water) → X^- (in glycerol + water); X = Cl, Br or I, on the mole-fraction scale in different glycerol + water mixtures at 25 °C (ΔG^0_t and ΔH^0_t, J mol^{-1} and ΔS^0_t, J mol^{-1} K^{-1})

	Wt% glycerol			
	5	10	20	30
X = Cl				
$10^{-3}\,\Delta G^0_t$	0.093	0.183	0.376	0.579
X = Br				
$10^{-3}\,\Delta G^0_t$	−0.154	−0.068	0.077	0.328
$10^{-3}\,\Delta G^0_{t,el}$	0.024	0.042	0.083	0.138
$10^{-3}\,\Delta G^0_{t,ch}$	−0.178	−0.110	−0.006	0.190
$10^{-3}\,\Delta H^0_t$	1.571	3.249	2.963	3.558
$10^{-3}\,\Delta H^0_{t,el}$	−0.022	−0.052	−0.092	−0.141
$10^{-3}\,\Delta H^0_{t,ch}$	1.593	3.301	3.055	3.699
ΔS^0_t	5.79	11.19	9.65	10.81
$-\Delta S^0_{t,el}$	0.154	0.313	0.589	0.934
$\Delta S^0_{t,ch}$	5.944	11.503	10.239	11.744
X = I				
$-10^{-3}\,\Delta G^0_t$	0.154	0.212	0.376	0.386
$10^{-3}\,\Delta G^0_{t,el}$	0.023	0.040	0.080	0.132
$-10^{-3}\,\Delta G^0_{t,ch}$	0.177	0.252	0.456	0.518
$10^{-3}\,\Delta H^0_t$	2.606	2.375	−2.246	−1.752
$-10^{-3}\,\Delta H^0_{t,el}$	0.021	0.050	0.089	0.135
$10^{-3}\,\Delta H^0_{t,ch}$	2.627	2.425	−2.157	−1.617
ΔS^0_t	9.262	8.683	−6.27	−4.58
$-\Delta S^0_{t,el}$	0.148	0.300	0.565	0.895
$\Delta S^0_{t,ch}$	9.410	8.983	−5.705	−3.685

glycerol + water mixtures are less than in water, which is in agreement with the behaviour exhibited by their counterpart, the silver–silver chloride electrode, studied in glycerol + water mixtures [1]. The E_m^0 values of the silver–silver bromide and silver–silver iodide electrodes were reported by Khoo [1] in 10, 20 and 30 wt% glycerol + water mixtures at 25 °C using boric acid–borate buffer cells. Their values are slightly different from the present values at the same temperature. Such differences might be due to the use of cells with liquid junctions, a cell different from that of the former worker. Dash and Nayak [3] reported the existence of such differences in the E_m^0 values of the silver–silver bromide electrode obtained from electromotive force measurements of two different cells buffered and unbuffered in formamide. However, the fair reproducibility of the present results and the smooth linear variation of the E_m^0 values with temperature suggest that the present set of data obtained at a number of temperatures are more reliable.

It is seen from Table 3 that while the standard Gibbs free energy changes increase, the standard entropy changes, which are all negative, increase, pass through a minimum at ca. 10% glycerol, and thereafter decrease with increasing glycerol concentration. The standard enthalpy changes for the Br^- ion are all negative and increase with increasing glycerol concentration whereas for the I^- ion they are positive and increase, pass through a maximum at ca. 10% and thereafter decrease with increasing glycerol content in the solvent mixture. The difference in sign and magnitude of the ΔH^0 values may be due to some structural effects. These effects can arise from either the combined effect of the solvent properties and solvation properties of the ions or the latter property alone in the different solvent mixtures. However, the solvent effect on the standard potentials of the silver–silver bromide or iodide electrode can be examined from the related quantities of Gibbs free energy of transfer of the Br^- or I^- ions from water to the solvent concerned, since the Gibbs free energy of transfer is an important index of the differences in interactions of the ion and the solvent molecules in the two different media.

As can be seen from Table 4, the standard Gibbs free energies of transfer, ΔG_t^0, for the Br^- ion appear to be negative for water-rich solvents, shifting to positive values for glycerol-rich solvents, whereas for the I^- ion, ΔG_t^0 values are negative and become increasingly negative as the proportion of glycerol increases. The negative values of ΔG_t^0 signify that the transfer of the Br^- ion from water to water-rich glycerol solvents and that of the I^- ion from water to any solvent is favourable, whereas the positive ΔG_t^0 values indicate that the Br^- ion is in a higher free energy state in glycerol-rich solvents than in water, and, therefore, the transfer process is not spontaneous. The Br^- ion is thus more strongly stabilised in water-rich solvents than in water, whereas for glycerol-rich solvents the solute is more strongly stabilised by solvation with water molecules. The I^- ion is in lower free energy states in the mixed solvents than in water. Thus, glycerol + water mixtures are more basic than water, and, further, the basicity increases with increasing the glycerol content in the solvent mixture.

A comparison of the ΔG_t^0 values for the transfer of the X^- ion (X = Cl, Br or I) from water to glycerol + water mixtures shows that the values of ΔG_t^0 for the Cl^- ion are all positive and increase with increasing glycerol concentration. The positive ΔG_t^0 values indicate that Cl^- is in a higher free energy state in the mixed solvents than in water and therefore the transfer process is not spontaneous. Thus, Cl^- is more strongly stabilised in water than in the mixed solvents.

The positive values of the standard transfer entropy, ΔS_t^0 (except for I^- for glycerol-rich solvents) indicate that the ions break the solvent structure more effectively in the mixed solvents than in water. Consequently, the degree of solvent orientation is less in the mixed solvents than in water. Thus, the net amount of order created by the Br^- or I^- ions is less in glycerol + water mixtures than in aqueous media, and, hence, the Br^- or I^- ions "break down more structure" in these mixed solvents, which are more structured than water. On the other hand, the negative ΔS_t^0 values of the I^- ion for 20 and 30 wt% glycerol mixtures indicate that the glycerol-rich solvents are less structured than water in the presence of a bigger anion like I^-. Hence, I^- is more effective at breaking the structure of water than glycerol-rich solvents. The positive ΔH_t^0 values (except for 20 and 30 wt% glycerol mixtures in the case of I^-) suggest that the transfer process is endothermic, because of the dehydration and then resolvation of the Br^- or I^- ions by glycerol.

A perusal of Table 4 shows that the values of $\Delta G_{t,el}^0$ are all positive and increase with increasing glycerol concentration in the solvent. The chemical part of the Gibbs free energy change of transfer, $\Delta G_{t,ch}^0$, which appears to be negative (except for a 30 wt% glycerol mixture in the case of Br^-) increases for the Br^- ion and decreases for the I^- ion with increasing glycerol content in the solvent. As $\Delta G_{t,ch}^0$ points to the acid–base properties of the mixed solvents, the negative $\Delta G_{t,ch}^0$ values indicate that the chemical reaction in the transfer process is spontaneous, and the spontaneity decreases in the case of the Br^- ion, but increases for the I^- ion with increasing glycerol concentration in the solvent. The negative values of $\Delta G_{t,ch}^0$ thus suggest that the mixed solvents possess a larger solvating capacity towards the ion concerned and are more basic than water. However, the decreasingly negative values of $\Delta G_{t,ch}^0$ with increasing glycerol content up to 20 wt% and finally positive values at 30 wt% glycerol suggest an increasingly strong affinity of the Br^- ion towards water than glycerol in the solution. The variation of both $\Delta H_{t,ch}^0$ and $\Delta S_{t,ch}^0$ values with solvent composition shows a similar trend to changes observed for ΔH_t^0 and ΔS_t^0 and thus may be explained in the same manner.

The values of the primary medium effect, which is represented by

$$\lim_{N \to 0} (\log {}^{s}\gamma_{w})[(E_N^0)_w - (E_N^0)_s]/2.3026(RT/F)$$

in various glycerol + water mixtures at 25 °C are shown in Table 5 along with those of the Cl^- ion for the sake of comparison. It is evident that the medium has a greater effect on the Cl^- ion as the glycerol concentration is gradually increased. The positive values of the primary medium effect suggest that the escaping tendency of the Cl^- ion is greater in glycerol + water mixtures than in the aqueous medium. Since the magnitude of the primary medium effect indicates the stabilisation of the ion in the solvent concerned, the resulting negative magnitude of this quantity for the Br^- ion in 5 and 10 wt% glycerol and for the I^- ion in all glycerol + water mixtures suggests that the escaping tendency of the Br^- and I^- ions is less in the mixed solvents than in pure water. This is consistent with the conclusions based on the fact that the Br^- and I^- ions are more strongly stabilised in these glycerol + water mixtures than in aqueous media. The reverse is true however, with the Br^- ion in glycerol-rich solvents where the primary medium effect values appear to be positive.

The thermodynamic solubility products, K^0_{so} of AgX (X = Cl, Br or I) in glycerol + water mixtures have been calculated at different temperatures from the values of standard potentials by means of the equation

$$\ln \mathrm{K}^0_{so}(\mathrm{AgX}) = \left[E^0_c(\mathrm{Ag/AgX}) - E^0_c(\mathrm{Ag/Ag^+})\right](F/RT) \tag{6}$$

where $E^0_c(\mathrm{Ag/AgX})$ is the standard molar potential of the Ag, AgX electrode and $E^0_c(\mathrm{Ag/Ag^+})$ is that of the silver electrode, obtained from the literature [2h]. The values for K^0_{so} on the molarity (K^c_{so}) and molality (K^m_{so}) scales are shown in Table 6 at the experimental temperatures. The data for K^m_{so} were calculated from K^c_{so}/ρ^2, where ρ is the density of the mixed solvent. The solubility product data in any solvent were fitted by least-squares to the equation

$$\log K^p_{so}(\mathrm{AgX}) = A/T + B \tag{7}$$

where $p = c$ or m and T (K) is any temperature. The constants A and B of eqn. (7) are shown in Table 7 along with the values of σ, the standard deviation of the least-squares fit: the correlation coefficient for these relations is 0.998.

TABLE 5

Primary medium effect, $\lim_{N\to 0} \log {}^s\nu_w$ (on the mole fraction scale) of the Cl^-, Br^- and I^- ions in various glycerol + water mixtures at 25 °C

X^-	Wt% glycerol			
	5	10	20	30
Cl	0.0162	0.0321	0.0659	0.1014
Br	−0.0270	−0.0118	0.0135	0.0575
I	−0.027	−0.0372	−0.0659	−0.0676

TABLE 6

Solubility product constants, on the molar (K_s^c) and molal (K_s^m) scales of AgX (X = Cl, Br or I) in glycerol + water mixtures at different temperatures

	t(°C)						
	5	10	15	20	25	30	35
5 Wt% glycerol, X = Cl							
$K_s^c \times 10^{10}$	0.692	1.12	1.77	2.76	4.23	6.28	9.13
$K_s^m \times 10^{10}$	0.66	1.07	1.70	2.67	4.11	6.13	8.95
X = Br							
$K_s^c \times 10^{13}$	1.2	2.79	4.15	7.45	12.98	21.99	36.38
$K_s^m \times 10^{13}$	1.14	2.67	3.99	7.20	12.60	21.45	35.69
X = I							
$K_s^c \times 10^{17}$	0.887	2.07	4.67	10.21	21.55	43.80	86.06
$K_s^m \times 10^{17}$	0.845	1.99	4.49	9.87	20.94	42.71	84.45
10 Wt% glycerol, X = Cl							
$K_s^c \times 10^{10}$	0.73	1.21	1.88	2.86	4.22	6.16	8.95
$K_s^m \times 10^{10}$	0.69	1.14	1.79	2.72	4.02	5.86	8.56
X = Br							
$K_s^c \times 10^{13}$	1.27	2.43	4.43	7.76	12.93	21.74	36.66
$K_s^m \times 10^{13}$	1.20	2.37	4.20	7.38	12.29	20.73	35.02
X = I							
$K_s^c \times 10^{17}$	1.06	2.45	5.37	11.23	22.75	46.03	90.72
$K_s^m \times 10^{17}$	1.00	2.32	5.09	10.69	21.66	43.95	86.77

20 Wt% glycerol, X = Cl							
$K_s^c \times 10^{10}$	0.74	1.15	1.78	2.82	4.28	6.50	9.26
$K_s^{m} \times 10^{10}$	0.67	1.04	1.62	2.56	3.90	5.92	8.45
X = Br							
$K_s^c \times 10^{13}$	1.36	2.42	4.31	7.76	13.39	24.29	39.08
$K_s^{m} \times 10^{13}$	1.24	2.20	3.91	7.06	12.19	22.16	35.64
X = I							
$K_s^c \times 10^{17}$	1.53	3.10	6.34	13.32	26.90	54.06	101.19
$K_s^{m} \times 10^{17}$	1.39	2.81	5.76	12.12	24.49	49.25	92.28
30 Wt% glycerol, X = Cl							
$K_s^c \times 10^{10}$	0.695	1.09	1.72	2.65	4.03	5.91	8.50
$K_s^{m} \times 10^{10}$	0.600	0.94	1.49	2.30	3.49	5.13	7.39
X = Br							
$K_s^c \times 10^{13}$	1.21	2.24	4.07	7.11	12.24	20.53	33.87
$K_s^{m} \times 10^{13}$	1.04	1.93	3.52	6.16	10.63	17.83	29.49
X = I							
$K_s^c \times 10^{17}$	1.46	3.20	6.76	13.91	27.97	54.27	102.34
$K_s^{m} \times 10^{17}$	1.26	2.77	5.85	12.05	24.27	47.17	89.09

TABLE 7

Constants of eqn. (7) for molar (c) and molal (m) scales in glycerol + water mixtures for different silver salts

	p	Wt% glycerol			
		5	10	20	30
X = Cl					
A	c	−3190.9325	−3067.2953	−3127.6715	−3098.3388
$B\times10^3$		1326.4422	915.3988	1121.6994	993.329
σ		0.053	0.051	0.052	0.052
A	m	−3231.231	−3111.5526	−3133.6948	−3109.986
$B\times10^3$		1449.2674	1044.2505	1100.8515	970.8408
σ		0.054	0.052	0.052	0.051
X = Br					
A	c	−4215.3833	−4161.3671	−4162.0267	−4131.3832
$B\times10^3$		2265.1748	2081.5632	2099.5742	1948.4394
σ		0.070	0.069	0.069	0.069
A	m	−4252.856	−4174.2593	−4167.8457	−4143.0305
$B\times10^3$		2378.3587	2105.2291	2078.3144	1925.9515
σ		0.071	0.070	0.070	0.074
X = I					
A	c	−5664.4455	−5509.9607	−5201.3893	−5261.6315
$B\times10^3$		3333.7819	2852.0634	1882.701	2097.7537
σ		0.094	0.091	0.087	0.088
A	m	−5701.8235	−5524.0328	−5207.3093	−5273.1803
$B\times10^3$		3446.785	2878.0037	1863.6518	2075.1474
σ		0.095	0.092	0.087	0.088

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